FY93 End of Fiscal Year Letter
(01 Aug. 1993 - 31 July 1994)

ONR CONTRACT INFORMATION

(1)

Contract Title: Damping Mechanisms in Nanostructured Materials

Performing Organization: Department of Chemical and Biochemical Engineering, University of California, Irvine, California, 92717-2575.

Principal Investigator: Enrique J. Lavernia, Associate Professor

Grant Number: N00014-93-1-1072

ONR Scientific Officer: Dr. Lawrence Kabacoff

A. Description of Scientific Research Goals

In recent years, research has indicated that nanocrystalline materials possess unique structural and mechanical properties. A nanocrystalline material is defined as a polycrystalline solid with an average crystal size of 5-10 nm. As a result of this small crystallite size, these materials contain a high volume fraction of grain boundaries and/or interfaces. This high percentage is the cause of the unique mechanical properties and also provides a new method for studying grain boundary behavior. Several methods, such as gas condensation, thermal crystallization and mechanical attrition, exist for the synthesis of nanocrystalline materials. The process of mechanical attrition uses high energy mechanical deformation to continuously fracture and weld the material, effectively refining the microstructure of the material. Research has demonstrated the synthesis of nanocrystalline alloys from elemental powders by this process of mechanical deformation. This process has also been shown to produce nanocrystalline microstructures from amorphous alloys, particularly metallic glasses. The advantage of this process lies is the ability to maintain the average crystallite size of about 10 nm. An understanding of the effect of mechanical deformation on the microstructural development of the elemental powders and on the crystallization behavior of the amorphous alloys should lead to the ability to control the resulting crystal size. To be useful for industrial applications, the nanocrystalline powder must be compacted into a bulk form without losing any of the benefits of the nanocrystalline microstructure. Therefore, an additional challenge is to control the thermal stability of the material during the compaction process and minimize the number of defects. Once synthesis and compaction of nanocrystalline materials is fully understood, significant research of the mechanical properties can be undertaken.

The objectives of the present ONR program may be described as follows: 1) determination of the mechanisms controlling the synthesis of nanocrystalline $Fe_{78}B_{13}Si_9$ from both elemental Fe, B, Si powders and Metglass 2605TCA ($Fe_{78}B_{13}Si_9$) during the process of high energy ball milling; 2) compaction of the milled powders by hot pressing and HIP; 3) determination of mechanisms governing the thermal stability of the milled powders using differential scanning calorimetry; and 4) the study of the effects of high volume fraction of grain boundaries or interfaces on the damping behavior of the nanocrystalline bulk material.

B. Significant Results

The research program was initiated on October, 1 1993; the present report covers the period from August 1, 1993 to July 31, 1994 (FY93). The principal research work conducted for this reporting period can be grouped into two categories: 1) determination of the mechanisms governing the crystallization behavior during mechanical alloying of Metglass 2605TCA alloy; 2) determination of mechanisms governing the synthesis of nanocrystalline powder during mechanical alloying of elemental powders. Results from the milling of elemental powders will be discussed in another report. Extensive thermal analysis using differential scanning calorimetry was completed to characterize the crystallization process observed during the mechanical milling process. X-ray diffraction and TEM analysis were also used in the identification of the microstructural details.

i. Mechanical milling of Metglass 2605TCA

Several experiments involving the mechanical milling of the metallic glass FeBSi alloy were conducted. The objective of these experiments was to determine the mechanisms governing the crystallization behavior of the material during the milling process. Previous research by others has described the crystallization of the amorphous material during this milling process but no acceptable explanation of the governing mechanisms has been offered. It has been suggested that there are two main factors governing the crystallization behavior: i) mechanical deformation of the amorphous material through collisions with the steel balls during the process and ii) thermal treatment applied to the materials as a result of the significant heat generated during the milling process.

Three mechanical milling experiments were conducted on the Metglass alloy with the following parameters: 1) ball milling in a Spex shaker mill in an atmosphere of argon with air cooling; 2) ball milling at room temperature, in a Szegvari attritor grinding mill in an atmosphere of air and 3) ball milling in the attritor grinding mill at cryogenic temperatures in an atmosphere of liquid nitrogen. Cryogenic milling is a mechanical alloying process in which the milling atmosphere is maintained at temperatures of about 77K (-196°C) and the material is constantly under an inert atmosphere of liquid nitrogen. The purpose behind the cryogenic experiment was to decrease the amount of heat generated during the milling in order to determine if

crystallization is a result of thermal treatment. The ball weight to sample weight ratio for each experiment was approximately 5:1.

Samples from each experiment were analyzed using a Perkin Elmer-Series 7 Differential Scanning Calorimeter (DSC) to determine the amount of amorphous phase remaining in the material. X-ray diffraction (XRD) analysis was performed on a Siemens D5000 Diffractometer, using Cu-Kα radiation, to determine the phases present after crystallization of the amorphous alloy. Samples were removed from the vial during the Spex milling experiment every half hour of milling. For the attritor milling in air, samples were removed at ten hour intervals and for the cryogenic run, every twenty hours.

The results from XRD studies indicated that there were two phases present after crystallization: α-Fe(Si) solid solution and Fe_2B. Thermal analysis, using DSC, of the as-received metglass showed the separate formation of two phases during thermal crystallization. Samples were analyzed at a continuous heating rate of 10°C/min from 350°C to 600°C. The formation of the phases was indicated by two exothermic peaks on a graph of ΔH (W/g) versus temperature (°C). The area under the peaks indicates the amount of amorphous phase remaining in the material.

Results from the Spex milling experiment showed a significant decrease in the amount of amorphous phase remaining after only 2.5 hours of milling. The area under the first peak (formation of α-Fe(Si) solid solution phase) decreased by approximately 90%. The second peak also had a decrease in total area, along with a shift to lower temperatures. Results from the attritor milling in air experiment also indicated a decrease in the percentage of amorphous phase remaining after milling for 40 hours. Both peaks appeared to decrease at the same rate with no shift to lower temperatures as seen in the Spex milling experiment. The amount of α-Fe(Si) phase increased to approximately 50 % after the 40 hours of milling. Similar results were obtained from the cryogenic experiment. After milling for 100 hours, DSC analysis indicated an increase in the amount of α-Fe(Si) phase of approximately 90%. Moreover, results for the formation of Fe_2B followed similar trends in both attritor experiments.

The crystallization rate for each of the experiments was compared by graphing the amount of crystalline phase versus the milling time. Figure 1 shows the results for the formation of the α-Fe(Si) phase for the milling performed in the attritor. The graph clearly shows a higher rate of crystallization for the milling done in the presence of oxygen. Figure 2 shows a similar trend for the crystallization rate of the Fe_2B phase. Results for the Spex milling experiment are shown in Figure 3. Crystallization of both phases occurs significantly faster than in the attritor milling experiments.

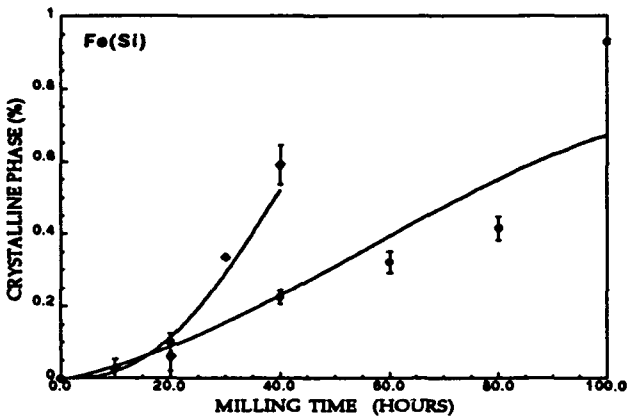

Fig. 1 Crystallization rate of α-Fe(Si) phase for cryogenic and air milling in the attritor.

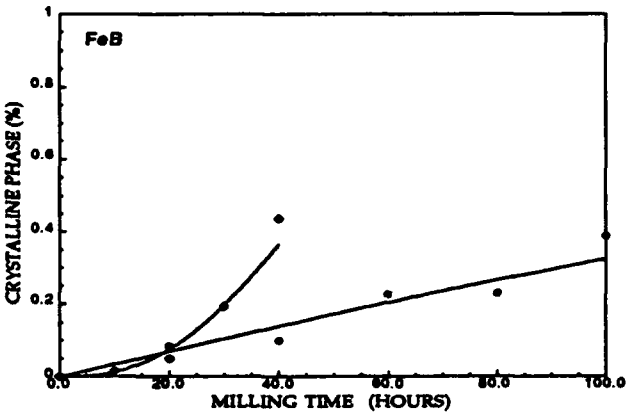

Fig. 2 Crystallization rate of Fe_2B phase for cryogenic and air milling in the attritor.

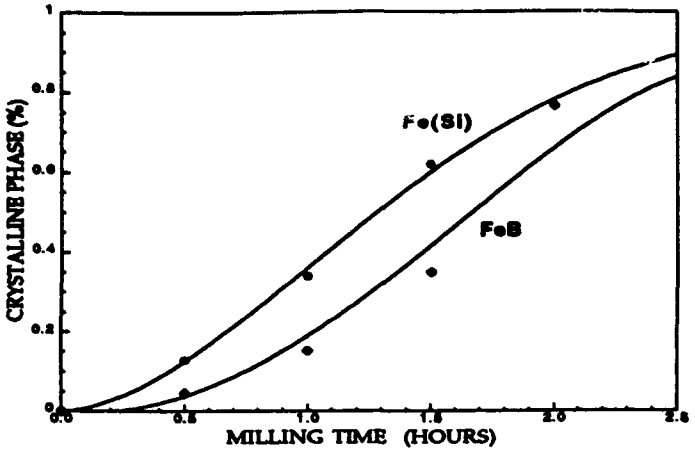

Fig. 3 Crystallization rate for both phases for Spex milling experiment

From the results of the cryogenic experiment, it is evident that crystallization occurs even in the absence of heat and in an minimal concentration of oxygen. Mechanical deformation may be the cause of the crystallization of the amorphous material during the ball milling process. The rate of crystallization increases significantly when milling in air due to an increase in the oxygen concentration in the milling atmosphere. The Spex milling experiment also revealed an increase in crystallization rate which was attributed to the increase in heat generated during the process. The effect of the oxygen concentration is assumed to be negligible since the milling was performed in an argon atmosphere.

Crystallization of amorphous metallic glass FeBSi during the high energy ball milling process occurs primarily through mechanical deformation, as indicated by the results obtained from the cryogenic milling experiment. Moreover, thermal treatment and the oxygen content in the milling atmosphere result in an increase in the rate of crystallization. The specific reasons for this phenomena are no yet clear and require further study.

C. Future Plans

(i). Detailed studies, using TEM, of the morphological development of the nanocrystalline structure during mechanical milling.

(ii). Change in activation energy due to mechanical milling.

(iii). Effect of mechanical milling on the magnetic properties, specifically Curie temperature.

(iv). Effect of oxygen content on the crystallization rate during mechanical milling.

(v). Compaction of milled powders by hot pressing or HIP.

(vi). Determination of the mechanisms governing grain growth during compaction of the nanocrystalline powders.

D. List of Publications/Reports/Presentations

1a. Papers Published in Refereed Journals

Benlih Huang & Enrique Lavernia, *Mechanical Alloying - A Synthesis Route Through Nanostructures*. Nanostructured Materials, vol. 4 no. 7 (1994)

1b. Papers Published in Refereed Conference Proceedings

Papers to be presented at the 1994 Fall MRS Meeting, Boston, Massachusetts:

i. The Study on the Synthesis of Nanocrystalline $Fe_{78}B_{13}Si_9$ by Mechanical Crystallization During Cryogenic Ball Milling at 77K. by Benlih Huang, Robert J. Perez, Paula J. Crawford, Adel Sharif and Enrique J. Lavernia.

ii. The Synthesis of Nanocrystalline $Fe_{78}B_{13}Si_9$ Powder by Mechanical Alloying of Elemental Powders by Robert J. Perez, Benlih Huang, Paula J. Crawford, Adel Sharif and Enrique J. Lavernia.

2. Non-Refereed Publications and Published Technical Reports

None for the present reporting period.

3. Presentations

3a. Invited

None for the present reporting period.

3b. Contributed

None for the present reporting period.

4. Books (and sections thereof)

None for the present reporting period.

E. List of Honors and Awards

Prof. E.J. Lavernia; Fellowship from the Iketani Science and Technology Foundation, Tokyo, Japan	1993
Prof. E.J. Lavernia; ASM International 1993 Bradley Stoughton Award for Young Teachers	1993
Prof. E.J. Lavernia; Elected to Who's Who in Science and Engineering	1993

Awards Received by Supervised Students

Name and Award	*Dates*
Robert J. Perez, Ph.D. candidate, Department of Defense, National Science and Engineering Fellowship for Ph.D. Studies	1992-1995
Scott Fable, Fluor Daniel Undergraduate Fellowship	1994
Don Baskin, Presidential Award for Excellence in Undergraduate Research (UCI Campus)	1994

F. Participants and Their Status

1. *Ph. D. Students*

2. *M.Sc. Students*
   i). Paula Crawford, M.Sc. candidate, joined the research program on January 1, 1994
3. *Undergraduate Students*

3. *Post-Doctoral Scientists*

4. *Technical Support*
   i). Mr. Irwin Sauer is a laboratory technician participating in our research program. 20% of his salary is supported by be present project.

G. Other Sponsored Research during FY93 (Dates; Annual Amount)

i). Principal Investigator, program entitled: "Synthesis of Metal Matrix Composites," Presidential Young Investigator Program, National Science Foundation; (January 1988 - December 1994; $67,000 per year matching Industrial funds).

ii). Principal Investigator, program entitled: "Microstructure Evolution and Mechanical Behavior of γ-TiAl processed by Spray Deposition," Air Force Office of Scientific Research; (September 9, 1994 - February 28, 1997; $110,000 per year).

iii). Principal Investigator, program entitled: "Semi-solid Processing of Ta-W Refractory Composites," Army Research Office; (June 1, 1992 - May 30, 1995; $100,000 per year).

iv). Co-Principal Investigator, program entitled: "Mathematical Modeling of Droplet Impact during Plasma Spraying," National Science Foundation; (December 1, 1992 - December 31, 1995; $68,000 per year).

v). Principal Investigator, NASA Langley program entitled: Mechanical Behavior of Spray Formed Al-Mg and AL-Li; (June 1994-May 1997; $68,000 per year).

H. Summary of FY93

Publications/Patents/Presentations/Honors/Participants (Number Only)

			ONR	non ONR
a.	Number of Papers Submitted to Refereed Journals but not yet published:		1	5
b.	Number of Papers Published in Refereed Journals:		1	4
c.	Number of Papers Published in Refereed Conference Proceedings:		0	6
d.	Number of Books or Chapters Submitted but not yet Published:		0	0
e.	Number of Books or Chapters Published:		0	1
f.	Number of Printed Technical Reports & Non-Refereed Papers:		0	3
g.	Number of Patents Filed:		0	5
h.	Number of Patents Granted:		0	1
i.	Number of Invited Presentations at Workshops or Prof. Societies:		0	4
j.	Number of Contributed Presentations at Workshops or Prof. Societies:		0	2
k.	Honors/Awards/Prizes for Contract/Grant Employees:		2	0
l.	Number of Graduate Students and Post-Docs Supported at least 25% this year on contract grant:			
	Graduate Students:	TOTAL	3	7
		Female	2	0
		Minority	1	0
	Post Doc:	TOTAL	1	2
		Female	0	0
		Minority	0	0
m.	Number of Female or Minority PIs or CO-PIs			
		New female	0	0
		Continuing Female	0	0
		New Minority	0	0
		Continuing Minority	1	0

GRANT NUMBER: N00014-93-1-1072

FORM A2-2

AUGMENTATION AWARDS FOR SCIENCE & ENGINEERING RESEARCH TRAINING (AASERT) REPORTING FORM

The Department of Defense (DOD) requires certain information to evaluate the effectiveness of the AASERT program. By accepting this Grant Modification, which bestows the AASERT funds, the Grantee agrees to provide the information requested below to the Government's technical point of contact by each annual anniversary of the AASERT award date.

1. Grantee identification data: (R & T and Grant numbers found on Page 1 of Grant)

a. UNIVERSITY OF CALIFORNIA, IRVINE
University Name

b. N00014-93-1-1072
Grant Number

c. MATLSYN 15-01
R & T Number

d. ENRIQUE LAVERNIA
P.I. Name

e. From: 8-1-93 To: 7-31-94
AASERT Reporting Period

NOTE: Grant to which AASERT award is attached is referred to hereafter as "Parent Agreement."

2. Total funding of the Parent Agreement and the number of full-time equivalent graduate students (FTEGS) supported by the Parent Agreement during the 12-month period prior to the AASERT award date.

a. Funding: $75,000.00

b. Number FTEGS: (1)

3. Total funding of the Parent Agreement and the number of FTEGS supported by the Parent Agreement during the current 12-month reporting period.

a. Funding: $75,000.00

b. Number FTEGS: (1)

4. Total AASERT funding and the number of FTEGS and undergraduate students (UGS) supported by AASERT funds during the current 12-month reporting period.

a. Funding: $53,300.00

b. Number FTEGS: (1)

c. Number UGS: (1)

VERIFICATION STATEMENT: I hereby verify that all students supported by the AASERT award are U.S. citizens.

Principal Investigator

3/12/94
Date